METHODS AND APPARATUS FOR DEPOSITING A THIN FILM ON A SUBSTRATE

Related Applications

The present application claims priority from Korean Patent Application No. 2002-86874, filed December 30, 2002, the disclosure of which is incorporated by reference herein in its entirety.

Field of the Invention

The present invention generally relates to an apparatus for manufacturing semiconductor devices and, more particularly, to an apparatus for depositing a metal oxide layer on a substrate.

Background of the Invention

Generally, Atomic Layer Deposition (ALD) is a method used for forming thin metal oxide layers, for example, an aluminum oxide layer, a hafnium oxide layer or the like. In ALD, a thin film is formed by serially providing reaction gases in a chamber. The thin film is formed on a surface of a substrate by reaction at the surface of the substrate, such that the film is formed to a uniform thickness. In addition, because the thin film develops proportionally to the amount of the reaction material, the thickness of the layer can be precisely controlled.

According to some methods, a metal oxide layer is formed by cyclically repeating ALD several times. Precursor and oxidant are serially introduced into the chamber in order to form the metal oxide layer having a desired thickness. The oxidant may include water vapor, hydrogen peroxide, ozone, etc., containing

oxygen atoms. Ozone has high reactivity and reacts with precursor coated on the substrate to form a thin, stable layer having good step coverage. Using ozone as the oxidant, however, has the disadvantage of a low deposition rate. If water vapor or hydrogen peroxide having high polarity are used as the oxidant, non-reacted water molecules or hydroxides may not be entirely removed. The residual water molecules or hydroxides may react with precursor provided in a subsequent cycle to form a new thin layer. In this case, the deposition rate of the thin film is high but the step coverage may be poor.

Recently, a method using both ozone and water vapor has been developed in order to satisfy the need for both high deposition rate and good step coverage.

Figure 1 is a schematic piping diagram showing a prior art apparatus for depositing a thin film that provides ozone together with water vapor.

Referring to **Figure 1**, the prior art apparatus for depositing a thin film includes an ozone provider **2**, a reaction gas provider **4**, a reaction chamber **10**, a selection transfer **3**, and a drainage pump **20**. The ozone provider **2** includes an ozone generator **30**, an ozone supply line **53** and a first process valve **1**. The ozone generator **30** generates ozone that is provided to the reaction chamber **10**. The ozone supply line **53** serves as a transfer path between the ozone generator **30** and the reaction chamber **10**. The first process valve **1** is installed in the ozone supply line **53** and permits or interrupts the flow of ozone.

The reaction gas provider **4** includes an oxidant container **50a**, a reaction material container **50b**, an inert gas generator **40** and supply lines. The oxidant container **50a** stores H_2O or H_2O_2 as a liquid oxidant source. The H_2O or H_2O_2 is present in the container **50a** in both liquid phase and vapor phase. The reaction material container **50b** stores precursor. The inert gas generator **40** generates inert gas that transports oxidant and reaction material to the reaction chamber **10**. The supply lines serve as supply paths for the inert gas, oxidant and reaction gas.

The reaction gas provider **4** further includes a first supply line **12**, a second supply line **22** and a first drainage line **42**. The first supply line **12** connects the inert gas provider **40** directly to the reaction chamber **10**. The second supply line **22** connects the inert gas generator **40** to the reaction chamber **10** through the oxidant container **50a**. The first drainage line **42** diverges from the second supply line **22** and connects the inert gas provider **40** directly to the drainage pump **20**.

The reaction gas provider **4** also includes a third supply line **32** and a second drainage line **52**. The third supply line **32** connects the inert gas generator **40** to the reaction chamber **10** through the reaction material container **50b**. The second drainage line **52** diverges from the third supply line **32** and connects the inert gas generator **40** directly to the drainage pump **20**.

First and second drainage valves **41** and **51** are installed in the first and second drainage lines **42** and **52**, respectively. The first and second drainage valves **41** and **51** interrupt or permit the flow of inert gas.

A first selection valve **21** and a second process valve **9** are installed in the second supply line **22**. The first selection valve **21** interrupts or permits the flow of inert gas to the oxidant container **50a**. The second process valve **9** interrupts or permits the flow of oxidant to the reaction chamber **10**.

A second selection valve **31** and a third process valve **19** are installed in the third supply line **32**. The second selection valve **31** interrupts or permits the flow of inert gas to the reaction material container **50b**. The third process valve **19** interrupts or permits the flow of reaction gas to the reaction chamber **10**.

The selection transfer **3** includes supply valves **5**, **15**, **25** and **35**, and bypass valves **7**, **17**, **27** and **37**. The supply valves **5**, **15**, **25** and **35** interrupt or permit the flow of oxidant and reaction gas to the reaction chamber **10**. The bypass valves **7**, **17**, **27** and **37** operate inversely to the supply valves **5**, **15**, **25** and **35** to exhaust the oxidant and the reaction gas to the drainage pump **20**.

As illustrated above, the prior art apparatus for depositing a thin film provides each of a first oxidant gas and a second oxidant vapor from a liquid source through independent supply lines to the reaction chamber. A plurality of process valves and supply valves are required to control the amounts of each of the oxidants. Accordingly, the breakdown frequency of one or more of the valves may be high and the valves may be complicated to control, thereby causing apparatus malfunction.

Summary of the Invention

According to embodiments of the present invention, an apparatus for depositing a thin film includes a reaction chamber, a reaction gas provider to supply a reaction gas and/or inert gas to the reaction chamber, an oxidant provider

to supply a first oxidant and a second oxidant to the reaction chamber, and an air drain to exhaust gas from the apparatus. The oxidant provider is operable to supply the second oxidant to the reaction chamber using the first oxidant as a transfer gas.

According to further embodiments of the present invention, an apparatus for depositing a thin film includes a reaction chamber, a reaction gas provider to supply a reaction gas and an inert gas to the reaction chamber, an oxidant provider to supply a first oxidant and a second oxidant to the reaction chamber, and an air drain to exhaust gas from the apparatus. The oxidant provider includes an oxidant generator to generate the first oxidant, an oxidant container to store the second oxidant, a first supply line to supply the first oxidant directly to the reaction chamber from the oxidant generator, and a second supply line fluidly connecting the oxidant generator to the reaction chamber via the oxidant container to supply the second oxidant to the reaction chamber using the first oxidant as a transfer gas.

According to further embodiments of the present invention, an apparatus for depositing a thin film includes: a reaction chamber; an oxidant generator to generate a first oxidant; an oxidant container; a second oxidant stored in the oxidant container; a reaction material container; a reaction gas stored in the reaction material container; an inert gas generator to generate an inert gas; a drainage pump to exhaust gas from the apparatus; a first supply line to supply the first oxidant directly to the reaction chamber from the oxidant generator; a second supply line connecting the oxidant generator to the reaction chamber via the oxidant container to provide the second oxidant to the reaction chamber using the first oxidant as a transfer gas; a third supply line to supply the inert gas directly to the reaction chamber from the inert gas generator; a fourth supply line connecting the inert gas generator to the reaction chamber via the reaction material container to supply the reaction gas to the reaction chamber using the inert gas as a transfer gas; and a drainage line diverging from the fourth supply line to exhaust the inert gas directly to the drainage pump.

According to further embodiments of the present invention, an apparatus for depositing a thin film includes: a reaction chamber; an oxidant generator to generate a first oxidant; an oxidant container to generate a second oxidant; a second oxidant stored in the oxidant container; a reaction material container; a

reaction gas stored in the reaction material container; an inert gas generator to generate an inert gas; a drainage pump to exhaust gas from the apparatus; a first supply line to supply the first oxidant directly to the reaction chamber from the oxidant generator; a second supply line connecting the oxidant generator to the reaction chamber via the oxidant container to provide the second oxidant to the reaction chamber using the first oxidant as a transfer gas; a third supply line to supply the inert gas directly to the reaction chamber from the inert gas generator; and a fourth supply line diverging from the third supply line and connecting the inert gas generator to the reaction chamber via the reaction material container to supply the reaction gas to the reaction chamber using the inert gas as a transfer gas.

According to method embodiments of the present invention, a method for depositing a thin film includes supplying a reaction a gas to a reaction chamber. A mixture of a first oxidant and a second oxidant is supplied to the reaction chamber. The first oxidant is used as a transfer gas for the second oxidant gas.

Objects of the present invention will be appreciated by those of ordinary skill in the art from a reading of the figures and the detailed description of the preferred embodiments which follow, such description being merely illustrative of the present invention.

Brief Description of the Drawings

Figure 1 is a schematic piping diagram showing a prior art apparatus for depositing a thin film;

Figure 2 is a schematic piping diagram showing an apparatus for depositing a thin film according to embodiments of the present invention;

Figure 3 is a schematic view of an oxidant container in accordance with embodiments of the present invention; and

Figure 4 is a schematic piping diagram showing an apparatus for depositing a thin film according to further embodiments of the present invention.

Detailed Description of the Preferred Embodiments

The present invention now will be described more fully hereinafter with reference to the accompanying drawings, in which embodiments of the invention are shown. This invention may, however, be embodied in many different forms

and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. In the drawings, the relative sizes of regions may be exaggerated for clarity. It will be understood that when an element such as a layer, region or substrate is referred to as being "on" or "connected to" another element, it can be directly on the other element or intervening elements may also be present. In contrast, when an element is referred to as being "directly on" another element, there are no intervening elements present except that, in the case of connecting piping or lines, there may be one or more valves, mass flow controllers or other flow control devices installed in the line between the referenced components.

Where valves are described herein as operating inversely, it is meant that when one valve is open the other valve is closed and vice-versa. According to some preferred embodiments, the valves are operated inversely automatically (*i.e.*, when the first valve is transitioned from closed to open, the other valve is automatically transitioned from open to closed, and vice-versa).

Figure 2 is a schematic pipe diagram showing an apparatus **150** according to embodiments of the present invention for depositing a thin film is shown therein. The apparatus **150** includes a reaction chamber **60**, an oxidant provider **63**, a reaction gas provider **73**, a selection transfer **83** and an air drain **93**.

The oxidant provider **63** includes an oxidant generator **80** and an oxidant container **100a**. The oxidant generator **80** generates a first oxidant and the oxidant container **100a** holds a second oxidant. The oxidant container **100a** provides an environment in which the second oxidant has a predetermined vapor pressure. According to some embodiments, the second oxidant is provided as a liquid source such that the second oxidant is present in the oxidant container **100a** in liquid phase.

A first supply line **92** connects the oxidant generator **80** directly to the reaction chamber **60**. A second supply line **62** connects the oxidant generator **80** to the reaction chamber **60** via the oxidant container **100a**.

A first process valve **91** is installed in the first supply line **92**. The first process valve **91** controls the flow of the first oxidant to the reaction chamber **60** from the oxidant generator **80**.

A first selection valve **61** and a second process valve **64** are installed in the second supply line **62**. The first selection valve **61** controls the flow of the first oxidant from the oxidant generator **80** to the oxidant container **100a**. The second process valve **64** controls the flow of the second oxidant and the first oxidant from the oxidant container **100a** to the reaction chamber **60** through the second supply line **62**.

The first selection valve **61** and the second process valve **64** operate inversely to the first process valve **91** to control the oxidant flow. When the first process valve **91** is opened and the first selection valve **61** and the second process valve **64** are closed, the oxidant from the oxidant generator **80** is provided directly to the reaction chamber **60**. When the first process valve **91** is closed and the first selection valve **61** and the second process valve **64** are opened, the first oxidant from the oxidant generator **80** flows into the oxidant container **100a** and carries or transfers the second oxidant from the oxidant container **100a** to the reaction chamber **60**. A mass flow controller (MFC) is installed between the oxidant generator **80** and the first process valve **91** and the first selection valve **61** in order to control the amount of the first oxidant supplied.

The oxidant provider **63** may supply one or more oxidant gases to the reaction chamber **60**, and one or more of these oxidant gases may be provided from gaseous and liquid sources. According to some embodiments, a plurality of oxidant generators and oxidant containers may be combined in a single apparatus to supply multiple oxidant gases from multiple gaseous and/or liquid oxidant sources. According to some embodiments, the first oxidant is a gas such as ozone or nitride monoxide. According to some embodiments, the second oxidant is provided as a liquid source such as liquid water or hydrogen peroxide.

Figure 3 is an enlarged, schematic view showing a suitable oxidant container **100a** in accordance with embodiments of the present invention. The arrangement and apparatus shown in **Figure 3** and described below may be used in other deposition apparatus, such as the apparatus **350** discussed hereinafter. Alternatively, this oxidant container **100a** may be replaced in the apparatus **150** with other suitable oxidant container apparatus.

Referring to **Figure 3**, the oxidant container **100a** includes a canister **200**, a pressurization line **62a** and a gas supply line **62b**. The canister **200** stores the second oxidant.

The second oxidant is provided as a liquid source **202**. According to some embodiments, the second oxidant is a liquid in its normal or natural state (*i.e.*, at standard temperature and pressure). The liquid source **202** is provided in the canister **200** up to an upper surface **204**. A headspace **206** is defined in the container **200** above the upper surface **204**. The pressure and temperature of the second oxidant in the canister **200** are maintained such that a selected amount of the liquid source **202** vaporizes to provide second oxidant in the vapor phase in the headspace **206**.

The pressurization line **62a** is inserted in the canister **200** with its open end positioned in the headspace **206** over the upper surface **204** of the liquid source **202** in the canister **200**. The pressurization line **62a** is connected to the oxidant generator **80** and ejects the first oxidant **210** from its open end and into the canister **200**. The gas supply line **62b** is also inserted in the canister **200** with its open end positioned in the headspace **206** over the upper surface **204** of the liquid source **202**. The gas supply line **62b** is connected to the process chamber **60**.

The second oxidant liquid source **202** is contained at a predetermined level and the pressure and temperature of the second oxidant in the canister are controlled to suitably manage the vapor pressure of the second oxidant. Ozone dissolves rapidly when it comes in contact with water. Therefore, as illustrated above, the openings of the pressurization line **62a** and the gas supply line **62b** may be positioned over the second oxidant liquid source **202** such that they are spaced apart from the upper surface **204** of the liquid source **202** a predetermined distance. The first oxidant **210** flows into the canister **200** through the pressurization line **62a**, mixes with the second oxidant vapor in the headspace **206**, and is exhausted from the canister **200** through the gas supply line **62b** together as a mixture **214** with the second oxidant vapor.

Referring back to **Figure 2**, the reaction gas provider **73** includes an inert gas generator **90**, a reaction material container **100b**, a third supply line **72**, a fourth supply line **82**, and a drainage line **102**. The inert gas generator **90** generates the inert gas that is provided to the reaction chamber **60**. The reaction

container **100b** holds reaction material which may be in the form of a liquid source. The third supply line **72** connects the inert gas generator **90** directly to the reaction chamber **60**. The fourth supply line **82** connects the inert gas generator **90** to the reaction chamber **60** via the reaction material container **100b**. The drainage line **102** diverges from the fourth supply line **82** and exhausts the inert gas directly to a drainage pump **70**.

A third process valve **71** is installed in the third supply line **72**. The third process valve **71** interrupts or permits flow of the inert gas from the inert gas generator **90** to the reaction chamber **60**.

A second selection valve **81** and a fourth process valve **84** are installed in the fourth supply line **82**. The second selection valve **81** interrupts or permits flow of the inert gas from the inert gas generator **90** to the reaction material container **100b**. The fourth process valve **84** interrupts or permits flow of the inert gas from the reaction material container **100b** to the reaction chamber **60**. In addition, a drainage valve **101** is installed in the drainage line **102** and operates inversely to the second selection valve **81** to exhaust the inert gas to the drainage pump **70** through the drainage line **102**.

When the drainage valve **101** is closed and the second selection valve **81** and the fourth process valve **84** are opened, the inert gas from the inert gas generator **90** transfers the reaction material of the reaction material container **100b** to the reaction chamber **60**. When the second selection valve **81** and the fourth process valve **84** are closed, the drainage valve **101** is opened and the inert gas generated from the inert gas generator **90** is exhausted directly through the drainage line **102** to the drainage pump **70**.

The selection transfer **83** includes supply valves **65**, **75** and **85** which interrupt or permit flow of the first oxidant, the second oxidant, the inert gas and the reaction gas. The first supply valve **65** controls flow of the first oxidant and the second oxidant (mixed with the first oxidant) into the reaction chamber **60**. The second supply valve **75** controls the flow of the inert gas into the reaction chamber **60**. The third supply valve **85** controls the flow of reaction gas into the reaction chamber **60**.

The selection transfer **83** further includes first, second and third bypass valves **67**, **77** and **87** that exhaust the first oxidant, the second oxidant, the inert gas

and the reaction gas through the drainage pump **70** by operating in inverse relation to each of the supply valves **65**, **75**, and **85**, respectively. The bypass valves **67**, **77**, and **87** each play a role in preventing rapid changes in the pressure of the supply line.

According to methods of the present invention, the third supply valve **85** is opened and the reaction gas is provided to the reaction chamber **60** from the reaction material container **100b**. A reaction gas layer, *i.e.*, a precursor layer, is formed on a substrate disposed in the reaction chamber **60**. Thereafter, the third supply valve **85** is closed and at the same time, the third bypass valve **87** is opened to exhaust the reaction gas to the drainage pump **70**. Then, the second supply valve **75** is opened and the inert gas flows into the reaction chamber **60** to purge the inside of the reaction chamber **60**.

Next, the first supply valve **65** is opened so that the first and second oxidants flow together (*e.g.*, as the mixture **214**) into the reaction chamber **60** to form a metallic oxide layer such as an aluminum oxide layer or a hafnium oxide layer on the substrate. The first supply valve **65** is then closed and at the same time the first bypass valve **67** is opened. Then, the second supply valve **75** is opened to purge the inside of the reaction chamber **60**.

The foregoing cycles are repeated several times to form a thin layer on the substrate. The first selection valve **61** and the first process valve **91** are suitably controlled to simultaneously provide the first and second oxidants as a mixture to the reaction chamber **60** or to provide only the first oxidant to the reaction chamber **60**.

In accordance with some embodiments of the present invention, the mixture **214** of the first and second oxidants is provided to the reaction chamber **60** via the line **62**, and thereafter the first oxidant is provided to the reaction chamber **60** alone (*i.e.,* without the second oxidant) via the line **92** only. In accordance with some methods of the present invention, water vapor and ozone are simultaneously provided to the reaction chamber in an initial step of the depositing process, and then only ozone is provided to the reaction chamber to achieve good step coverage. Such methods may be employed to achieve rapid deposition.

Figure 4 is a schematic pipe diagram showing an apparatus for depositing a thin film according to further embodiments of the present invention.

Referring to **Figure 4**, the apparatus includes a reaction chamber **360**, an oxidant provider **363**, a reaction gas provider **373**, a selection transfer **383**, and an air drain.

The oxidant provider **363** includes an oxidant generator **380** and an oxidant container **300a**. The oxidant generator **380** generates a first oxidant that is provided to the reaction chamber **360**. The oxidant container **300a** contains a second oxidant. The oxidant container **300a** provides an environment in which the second oxidant has a predetermined vapor pressure. According to some embodiments, the second oxidant is provided as a liquid source such that the second oxidant is present in the oxidant container **300a** in liquid phase. According to some embodiments, the oxidant container **300a** corresponds to the oxidant container **100a** described above with reference to **Figure 3**.

A first supply line **392** connects the oxidant generator **380** directly to the reaction chamber **360**. A second supply line **362** connects the oxidant generator **380** to the reaction chamber **360** via the oxidant container **100a**.

A first process valve **391** and second process valve **364** are installed in the first supply line **392**. The first process valve **391** interrupts or permits flow of the first oxidant from the oxidant generator **380** to the reaction chamber **360**. The second process valve **364** interrupts or permits flow of the second oxidant and the first oxidant from the oxidant container **300a** to the reaction chamber **360**. The first selection valve **361** and the second process valve **364** operate inversely to the first process valve **391**.

According to some embodiments, the first oxidant may be a gas such as ozone or nitride monoxide. According to some embodiments, the second oxidant is provided as a liquid source such as liquid water or hydrogen peroxide.

The second oxidant is transferred to the reaction chamber **360** by the first oxidant that flows into the oxidant container **300a**. The oxidant provider **363** may provide one or more oxidant gases to the reaction chamber **360**, and one or more of these oxidant gases may be provided from gaseous and liquid sources. According to some embodiments, a plurality of oxidant generation devices and a plurality of oxidant containers may be provided and suitably combined to supply multiple oxidant gases from multiple gaseous and/or liquid oxidant sources.

The reaction gas provider **373** includes an inert gas generator **390**, a reaction material container **300b**, a third supply line **372** and a fourth supply line **382**. The inert gas generator **390** generates inert gas that is provided to the reaction chamber **360**. The reaction container **300b** contains reaction material. The third supply line **372** connects the inert gas generator **390** directly to the reaction chamber **360**. The fourth supply line **382** is diverged from the third supply line and connected to the reaction chamber **360** via the reaction material container **300b**.

A third process valve **371** is installed in the third supply line **372**. The third process valve **371** interrupts or permits the flow of inert gas that flows to the reaction chamber **360** from the inert gas generator **390**. A second selection valve **381** and a fourth process valve **384** are installed in the fourth supply line **382**. The second selection valve **381** interrupts or permits the flow of the inert gas from the inert gas generator **390** to the reaction container **300b**. The fourth process valve **384** interrupts or permits the flow of reaction gas from the reaction container **300b** to the reaction chamber **360**.

The selection transfer **383** includes supply valves **365** and **385** that interrupt or permit flow of the first and second oxidants, the inert gas and the reaction gas into the reaction chamber **360**. The first supply valve **365** interrupts or permits the flow of the first oxidant and second oxidant (mixed with the first oxidant) into the reaction chamber **360**. The second supply valve **385** interrupts or permits the flow of the inert gas and the reaction gas into the reaction chamber **360**.

The selection transfer **383** further includes first and second bypass valves **367** and **387** that exhaust the first and second oxidants, the inert gas and the reaction gas by operating inversely to each of the supply valves **365** and **385**. The bypass valves **367** and **387** may prevent drastic variations in the pressure in the supply lines.

According to methods of the present invention, the second selection valve **381** and the fourth process valve **384** are opened and the third process valve **371** is closed to provide reaction gas to the reaction chamber **360** from the reaction material container **300b**. The second supply valve **385** is opened so that the reaction gas flows into the reaction chamber **360** to form a reaction gas layer (*i.e.*, a precursor layer) on the substrate disposed in the reaction chamber **360**. Thereafter, the second supply valve **385** may be closed and the second bypass

valve **387** immediately opened to exhaust the reaction gas directly to the drainage pump **370**.

The inert gas may be flowed into the reaction chamber **360** to purge the inside of the chamber **360** by closing the second selection valve **381** and the fourth process valve **384**, opening the third process valve **371**, and opening the second supply valve **385**. The second supply valve **385** is closed and the second bypass valve **387** is opened at the same time so that the inert gas is exhausted directly to the drainage pump **370**.

Thereafter, the first supply valve **365** is opened so that the first and second oxidants flow together (*e.g.*, as a mixture) into the reaction chamber **360** and react with the precursor layer on the substrate to form a metal oxide layer such as an aluminum oxide layer or a hafnium oxide layer. As soon as the supply valve **365** is closed, the first bypass valve **367** is opened and the second supply valve **375 [?]** is opened to purge the inside of the reaction chamber **360**.

The cycle explained above may be repeated several times to form a thin layer on the substrate. The first selection valve **361** and the first process valve **391** are suitably controlled to provide first and second oxidants to the reaction chamber **360** or to provide only the first oxidant to the reaction chamber **360**.

Apparatus in accordance with the present invention may be used to transfer an oxidant from a liquid source to a process chamber using an oxidant gas as a transfer gas, thereby allowing for a reduction in the number of valves installed in an oxidant supply line or lines. The oxidant gas used as the transfer gas may be provided to the process chamber with the second oxidant through a supply line, and the oxidant gas and the oxidant from the liquid source may be provided together to the process chamber through the same line. As a result, the risk of valve malfunction in the supply line may be decreased, such that the process can be stably performed.

The foregoing is illustrative of the present invention and is not to be construed as limiting thereof. Although a few exemplary embodiments of this invention have been described, those skilled in the art will readily appreciate that many modifications are possible in the exemplary embodiments without materially departing from the novel teachings and advantages of this invention. Accordingly, all such modifications are intended to be included within the scope of this

invention. Therefore, it is to be understood that the foregoing is illustrative of the present invention and is not to be construed as limited to the specific embodiments disclosed, and that modifications to the disclosed embodiments, as well as other embodiments, are intended to be included within the scope of the invention.